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Sol-Gel Template Synthesis and Photocatalytic Activity of TiO_2 Nanofibrils Loaded on Al_2O_3 Template

Yuan GAO, Wei YU, Meng Ke LI, Hu Lin LI*

Department of Chemistry, Lanzhou University, Lanzhou 730000

Abstract: TiO_2 nanofibrils were prepared within the pores of alumina template membrane by use of sol-gel chemistry. The TiO_2 nanofibrils have good crystallinity and size. There is agglomeration free among the particulates of TiO_2 and the fibrils show high catalytic activity.

Keywords: TiO_2 nanofibrils, photocatalysis, template-synthesis method.

During recent decades, photocatalytic degradation of various toxic organic compounds has been proposed as a viable process to detoxify drinking water[1]. Environmental purification using TiO_2 photocatalysts has attracted a great attention with the increasing number of environmental problems in the world[2]. As photocatalysts are often applied as suspensions, many problems associated with catalyst leaching, settling, floatation and the separation of catalyst during post treatment. These hinder their wide scale application in industry. Therefore, catalyst immobilization related research has attracted wide attention[3]. Simple coating[4-6] of the catalyst over glass, zeolite, silica, and ceramic, however, often leads to catalyst leaching and dissolution. On the other hand, the generally used sol-gel method induces agglomeration of the particulates of the catalyst film in the burning process. In this work we prepared TiO_2 nanofibrils by use of sol-gel chemistry within the pores of alumina template membrane to solve above problems. This material binds to alumina firmly, and has the advantages of good crystallinity and size. It is easily recyclable. The photocatalytic activities of TiO_2 nanofibrils/Al_2O_3 and TiO_2/glass plate were measured using an acridine dye solution as a model.

Microporous anodic aluminum oxide (AAO) films were prepared by anodic oxidation of electropolished aluminum plate at a cell voltage of 80 V in 0.5 mol/L phosphoric acid at 25°C for 1.5 h[7]. The porosity of the anodic membrane consisted of an array of parallel and straight channels with a diameter of about 80 nm, and the film diameter and thickness were 15 mm and about 20 μm, respectively. TiO_2 fibrils were prepared using a sol-gel method similar to that described by Lakshmi *et al.*[8]. Firstly, the TiO_2 sol was prepared. Then the AAO films were dipped into this sol for an immersion time 5 to 60s. After immersion, the membrane was removed from the sol, dried at room

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*E-mail: liuht@lzu.edu.cn

temperature and then heated in a tube furnace. The formed TiO_2 nanofibrils were characterized by atomic force microscope (AFM). **Figure 1** shows the AFM image of porous AAO template with a pore diameter of about 80 nm and a pore density of about 10^{10}-10^{11} cm^{-2}. Perfect hexagonal pore arrays can be observed within domains of microsize, which are separated from neighboring alumina domains with a different orientation of the pore lattice by grain boundaries. The AFM image of TiO_2 deposited on the porous AAO template is shown in **Figure 2**. Discontinuous distribution of uniform and small grain TiO_2 with average particle size of 80 nm on the surface of AAO template was obtained.

Figure 1 Surface morphology by AFM of AAO template

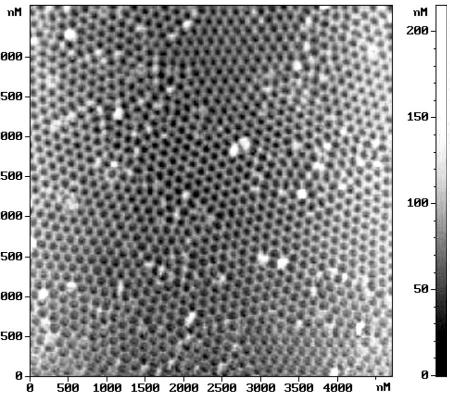
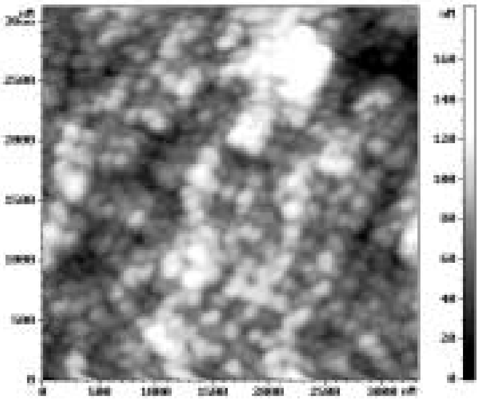
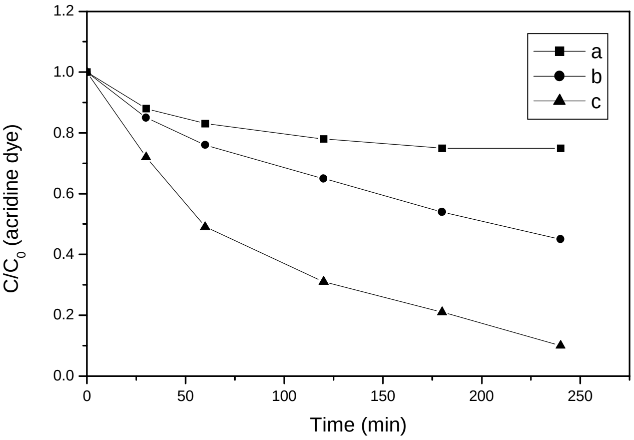


Figure 2 Surface morphology by AFM of TiO_2 nanofibrils/Al_2O_3 film



The photodegradation of acridine dye in aqueous solution under visible light irradiation with a medium pressure mercury lamp was carried out to test the photocatalytic activities of TiO_2 nanofibrils/Al_2O_3. In comparison, glass plate supported TiO_2 were tested under the same condition. The degradation of acridine dye was monitored by UV-Vis spectroscopy. The results were illustrated in **Figure 3**. In the absence of TiO_2, the loss of acridine dye from the solution during irradiation was very slow (curve a) compared with other two curves, indicating that the degradation of acridine dye was a TiO_2-associated photocatalytic process. The curve c in **Figure 3** is for the solution that contained the fibrillar TiO_2/Al_2O_3 photocatalyst. A rapid (relative to the TiO_2/glass film catalyst, curve b) decrease in acridine dye concentration was observed. The observed first-order photodegradation rate constant of fibrillar TiO_2/Al_2O_3 photocatalyst is 9.1×10^{-3} min^{-1}, larger than that of TiO_2/glass film (3.2×10^{-3} min^{-1}).

Figure 3 The photodegradation of acridine dye (2.74×10^{-5} mol/L) under irradiation by visible light (wavelengths > 470nm)



(a) no photocatalyst, (b) the thin-film TiO_2/glass photocatalyst,
(c) the TiO_2 fibriliar/Al_2O_3 film photocatalyst.

Our results demonstrate that the rate of photocatalytic degradation of acridine dye is dependent on the template on which TiO_2 is loaded. AAO is a better template than glass plate. The explanation lies in the following facts: Photocatalytic chemical reactions occur on the surface of TiO_2. Therefore catalyst with larger surface areas is more efficient. Loading TiO_2 on glass plate unavoidably led to aggregation of TiO_2 particulates due to long-time heating-treatment, and consequently decreased the surface active sites. This aggregation does not occur to TiO_2 loaded on AAO, as shown in **Figure 2**. The nanoparticles can be seen clearly uniformly distributed over the AAO template. The porous structures on the surface of alumina template help to fix TiO_2 particles within the nanosize pores, preventing TiO_2 from aggregation with one another during heating process. This porous structure also strengthens the binding of TiO_2 on AAO, thus the TiO_2 fibriliar/Al_2O_3 film is very stable. No catalyst desquamating was observed during our experiments.

In conclusion, the AAO supported nanoparticles TiO_2 was prepared and its photocatalyzing effect in photodecomposition of organic substances in water phase was found. The supporting materials were proved to play an important role to affect the photocatalyzing activity of the TiO_2 nanofibriliars. The crystalline phase, particle shapes and the way the particles array of TiO_2 nanofibriliars are also the significant factors, affecting the catalytic activity. This work might be helpful to develop new, highly efficient immobilized photocatalysts in further studies.

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